Spray Freeze Granulation of Submicron Alumina and its Sintering Behavior via Spark Plasma Sintering

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Abstract:
Spray freeze granulation is an improved method based on spray granulation, solving many limitations of spray granulation. In this work, spray freeze granulation of submicron alumina is performed to explore the possibility of industrial-scale production of dense alumina via spark plasma sintering. Powder pretreatment such as sedimentation and the selection of granules with the appropriate size are employed for the maximum use of the high qualified as-prepared granules and granule sliding, which would provide a guidance for the industrial-scale production. Debound granules were densified via SPS and the corresponding sintering behaviors such as the recorded shrinkage and shrinkage rate were discussed. The comparison of sintering behaviors between granulated and as-received powder are conducted to identify the role of spray freeze granulation in sinterability for dense alumina. The Vickers hardness (Hv) and the fracture toughness (KIC) of the freeze granulated body are higher than the corresponding properties of the as-received body due to the more homogenous microstructure with little agglomeration in the particle packing after freeze granulation.

Keywords: Alumina; Spray freeze granulation; Spark plasma sintering; Sintering behavior

1. Introduction

It is well known that fine ceramic materials are very appealing for high-performance applications due to their temperature and corrosion resistance, low density, high stiffness, hardness, and strength [1]. Unfortunately, owing to their extremely high specific surfaces and their high surface-to-volume ratios, superfine ceramic powders show a strong tendency to agglomeration and poor flowability [2]. For improved properties of these powders during storage, transport, shaping, the classical approach of granulation is necessary [3]. Powder granules rather than powder itself are the most popular starting material for the dry pressing process. Granules posses several merits, such as giving flowability to fine powders in a die and avoiding generation of floating dust [4,5]. Among various kinds of shaping techniques, dry pressing is considered to be one of the most popular forming techniques for ceramic component manufacture owing to its attractive attributes, including ease of automation, relatively low energy consumption, high material utilization, and ability to convert powders into moderately complex shapes with high precision and close tolerances at low cost [6-8]. As it is for the process of compaction, the granules are required to break down into their primary particles without remnants of the initial granule structure present in the final green body.

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Single remnant can result in a severe loss of strength by acting as a Griffith flaw [6, 9, 10]. Usually, powder granules are prepared using a spray-drying (SD) process, in which an aqueous slurry with an organic binder is sprayed into hot air and the sprayed droplet is dried to a granule [11-12]. However, this process introduces serious disadvantages. During drying, moisture evaporates from the surface of the slurry droplet. At the same time, the binder solution moves toward the surface from the inside of the droplet [4]. During moisture evaporation, the organic binder remains at the surface and produces a surface-segregated layer after the granule is dried, making granules harder or impossible to deform into powder particles during later compaction. This segregated binder layer remains after the pressing process and can be observed in the sintered body. The trace of binder acts as a strength-limiting defect and decreases the reliability of the produced ceramics [13].

Spray freeze drying (SFD) is an improved method based on spray drying, which combines the advantages of a conventional granulation by spray drying and a sublimation drying process [2], solving many limitations of spray drying. Freezing being a fast process, diffusion dynamics are insufficient to induce any binder migration, thereby better preserving the granule homogeneity. Additionally, the granules don’t shrink during the whole process and therefore maintain their shape and powder density, consequently allowing higher granule deformability compared to spray drying [3, 14].

In this article, spray freeze granulation of submicron alumina is performed to explore the possibility of industrial-scale production of dense alumina via spark plasma sintering. Sedimentation and the selection of granules with the appropriate size are both beneficial for the maximum use of the highly qualified as-prepared granules and granule sliding, which will provide a guidance for the industrial-scale production.

2. Experimental procedure

The entire technological profile is shown in Fig.1.

![Fig. 1. The whole technological profile of the experimental procedure.](image)

2.1 Suspension preparation

The ceramic powder (AAO4, Sumitomo, Japan) used was a commercial α-alumina
(Purity no less than 99.99%) with Brunauer-Emmett-Teller specific area of 4.2 m$^2$/g. Fig. 2(a) and Fig. 2(b) are the respective SEM microstructure of the as-received particles and the size distribution which is evaluated by SEM. The solid loading of the suspension was 30 vol%. Polyethylene glycol (PEG) and polyvinyl alcohol (PVA) were used as the lubricant and binder respectively with the respective concentration of 0.34 g/ml and 0.15 g/ml in the aqueous solution. The total percentage of PVA and PEG is 1.5 wt% among the whole powder with the weight ratio of 3 to 2. Two commercial dispersants (Dolapix CE64 and Darvan 821a) combined with citric acid were adopted to stabilize the suspension at pH 6. After that, the suspension was ball milled for 24 h using translucent alumina balls.

**Fig. 2.** (a) SEM microstructure of the as-received particles; (b) the size distribution of the as-received particles.

### 2.2 Sedimentation

Sedimentation is adopted to remove agglomerates and impurities. The sedimentation time could be calculated according to the following equation [15]:

$$U_0 = \frac{2(\rho_S - \rho_{\text{water}})}{9\eta_o} \cdot a^2 g$$  \hspace{1cm} (1)

$$\frac{U}{U_o} = (1 - \phi)^n$$ \hspace{1cm} (2)

This equation describes a model where a spherical particle of density $\rho_S$ and radius $a$ were released into a viscous fluid of viscosity $\eta_o$ and density $\rho_{\text{water}}$, where momentarily accelerates and then decreases at $U_o$ ($U_o$ is the constant terminal velocity). In addition, $\phi$ is the solid loading of the suspension and $n$ is exponential factor (usually =6.55). Agglomerates and impurities with the size bigger than 2 $\mu$m are expected to be removed, hence $a=1$ $\mu$m.

### 2.3 Spray freeze granulation

Suspension was placed into a beaker and was stirred at 200–400 rpm depending on the viscosity of the suspension. The pump speed was set to: 1 ml/min, the gas pressure was set to: 0.4 bar and the flow rate was set to: 40 rpm. After that, the freeze sprayed powder was placed in the fridge-freezer set at -20°C and granules were immediately formed.

Finally, the solid-state granules were placed in freeze dryer for 24 h. During this procedure, solid-state binders transformed into a liquid one while the final granules formed.
2.4 Sieving

Granules were first sieved by griddles with different meshes to confirm the optimal granule size. For SPS, granules were sieved and then heated at 500 °C for 5h to remove binders.

2.5 Shaping and Sintering

The shaping and sintering was accomplished using SPS apparatus (Dr Sinter 2050, Sumitomo Coal Mining Co., Tokyo, Japan). A bath of 3g of the alumina granulated powder was loaded in a cylindrical graphite die with an inner diameter of 20 mm. After applying a pressure of 100 MPa, samples were heated from room temperature to 600 °C for 3 min and then raised to the final temperature with the heating rate of 100 °C/min.

2.6 Characterization

The relative density was measured by Archimedes method taking 3.98g/cm$^3$ as the theoretical density (T.D.% in the following text) of alumina. A field emission scanning electron microscope (FE-SEM) (JSM-7000F, JEOL, Tokyo, Japan) was employed to investigate the microstructure features, i.e., the size and morphology of the starting powder, the granules and the pores. The particle size and its distribution are statistic values evaluated through the SEM image via the software of Nano Measurer. The Hausner ratio and Carr index were adopted to characterize the flowability of the granules. The smaller the Hausner ratio and Carr index, the better the flowability. The Hausner ratio and Carr index were measured as per the relevant British Standard [16]. Briefly, the untapped/initial density, $D_i$, was obtained by allowing it to fall freely into a stationary container, avoiding vibrations. To measure the tap density, $D_t$, the powders were tapped 1000 times with a constant amplitude of 3 mm; it was observed that there was no appreciable change in the tap density after approximately 300 taps. The Hausner ratio and Carr index were then calculated from [6]:

$$Hausner - ratio = \frac{D_i}{D_u}$$

(3)

$$Carr - index = 100 \cdot \frac{D_u - D_t}{D_i}$$

(4)

Before the hardness and toughness measurements, the specimens were carefully polished, by standard diamond polishing techniques, down to a diamond particle size of 1 μm. The hardness ($H_v$) and fracture toughness ($K_{IC}$) at room temperature were evaluated by the Vickers indentation technique at a load of 98 N, according to Anstis et al [17]. More than five indents were made in a row at the middle of each sample (to minimize near-surface effects). A Young’s modulus value of 380 GPa was used for Al$_2$O$_3$ in the calculations. Only samples with >99% of the theoretical density (TD=3.98 g/cm$^3$) were considered fully dense and were used for measuring hardness and fracture toughness.

3. Results and discussion

3.1 Sedimentation

The SEM global field version of the as-received particles after the ultrasonic treatment is shown in Fig. 3(a). It could be seen from Fig. 3(a) that there are a large number of agglomerates (marked by red circles), which will be harmful to the following granulation and sintering. The method of sedimentation is adopted to deal with the suspension in order to eliminate agglomerates. The particle size distribution after sedimentation is shown in Fig.
3(b). It indicateds that agglomerates with the particle size bigger than 2 μm have been removed, which is in good agreement with the experimental expectation. Fig. 3(c) depicts the SEM microstructure of the residue dropped from the suspension after sedimentation and the large region in red circle seems to be the fragment dropped from the milled balls.

3.2 Spray freeze granulation

The microstructure of the as-prepared granules after SFD is shown in Fig. 4(a). The microstructure shows a large number of different types of agglomerates (marked by red circle in Fig. 4(a)). Fig. 4(b) represents the microstructure of the fracture surface of the collapsed granule, which implies that granules are very soft, easy to be crushed and suitable for dry pressing.

3.3 Sieving

Granules were sieved by griddles with different meshes. The mass ratio of granules with different size is shown in Tab. I. The flowability of granules with different size is shown in Tab. II. It can be seen from Tab. II that granules with the particle size smaller than 150μm shows the best flowability due to its lowest Hausner ratio and Carr index [6]. Combined with Tab. I, the mass ratio of granules with the particle size smaller than 150 μm is close to 85%, occupying the majority of the whole as-prepared granules. Therefore, granules with the size bigger than 150μm will be abandoned due to their poor flowability.
The microstructures of granules with different size range are shown in Fig. 5. It could be seen that the shape of granules (d<150 μm) is regular without apparent agglomerates (Fig. 5(c, d)), which is proper for dry pressing. Though the dispersity of granules (d<36 μm) is fine (Fig. 5(d)), due to its low weight, the dispersity of the corresponding granules is not satisfactory on the contrary. As a result, the combination of middle-sized granules (36μm<d<150μm) and small-sized granules (d<36 μm) seems to be the best choice.

**Tab. I** The mass ratio of granules with different size

<table>
<thead>
<tr>
<th>Diameter (μm)</th>
<th>Mass ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d&lt;36μm</td>
<td>14.40</td>
</tr>
<tr>
<td>36μm &lt;d&lt;150μm</td>
<td>69.39</td>
</tr>
<tr>
<td>150μm&lt;d&lt;200μm</td>
<td>5.27</td>
</tr>
<tr>
<td>d&gt;200μm</td>
<td>10.94</td>
</tr>
</tbody>
</table>

**Tab. II** The flowability of granules with different size

<table>
<thead>
<tr>
<th>Granule size</th>
<th>Fill density(g/cm³)</th>
<th>Tap density(g/cm³)</th>
<th>Hausner ratio</th>
<th>Carr index</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared</td>
<td>0.74</td>
<td>0.91</td>
<td>1.23</td>
<td>18.69</td>
</tr>
<tr>
<td>d&gt;150μm</td>
<td>0.78</td>
<td>0.93</td>
<td>1.19</td>
<td>16.13</td>
</tr>
<tr>
<td>d&lt;150μm</td>
<td>0.65</td>
<td>0.71</td>
<td>1.09</td>
<td>8.45</td>
</tr>
</tbody>
</table>

**Fig. 5.** The microstructures of granules with different size range: (a) d> 200μm; (b) 150μm<d<200μm; (c) 36μm <d<150μm; (d) d<36μm.
3.4 Absorption mode

The microstructures at different magnification of granules (d<150μm) are shown in Fig. 6. It is shown that small granules absorb on big granules and it is believed that such absorption mode is beneficial for granule sliding and deformability, resulting in excellent flowability of granules. In addition, the inner whole structure of the granule is quite homogenous, which is exactly the advantage of SFD, avoiding the hollow structure caused by SD [6]. The binders appear filiform, making the original powder connected with each other closely.

![Fig. 6. The microstructures at different magnification of granules (d<150μm).](image)

3.5 Sinterability via Spark plasma sintering

The recorded real-time sintering curves are shown in Fig. 7(a), where the shrinkage and linear shrinkage rate are plotted versus temperature after removing the contribution of the thermal expansion of the graphite tool set. It appears that the shrinkage is accelerated by the increment of temperature. The shrinkage rate reaches the first maximum, 1×10⁻³s⁻¹, at 640 °C, whereas it dramatically drops to 3×10⁻³s⁻¹ at about 720 °C. The second peak of shrinkage rate occurs in the temperature range from 1100 °C to 1150 °C, which is approximately 6×10⁻³s⁻¹~7×10⁻³s⁻¹.

The relationship among the recorded shrinkage, the shrinkage rate and the relative density is shown in Fig. 7(b). Densification increases with the increment of the density, which could be linear fitted by the following line:

\[ y = 0.0689x - 0.06835 \]

The shrinkage rate firstly raises and then reduces with the increment of the relative density, which achieves the maximum value at the relative density of 83T.D.%. The curve could be polynomial fitted and the fitting equation is as follows:
The comparison of sintering behaviors between the granulated and as-received powder from 1000 °C to 1500 °C is shown Fig. 8. The initial densities of both powders at 1000 °C are 69.6 T.D.% and 64.3 T.D.% respectively. The densities increase with the increment of temperature for both powders and appear similar growth trend. The sintering curve of the as received powder seems to fall behind the freeze granulated powder. Both powders obtain full density at 1350 °C. It can be concluded that the process of freeze granulation could avoid agglomeration and leads to more homogenous microstructure of the green body, which promotes the sintering of alumina compact [18-20].

\[ y = -0.0621 + 0.0087 \exp \left( -0.5 \left( \frac{x - 0.8605}{0.1033} \right)^2 \right) \]

Fig. 7. (a) The recorded shrinkage and shrinkage rate during spark plasma sintering versus temperature; (b) the relationship among the recorded shrinkage, the shrinkage rate and the relative density.

Fig. 8. The comparison of sintering behaviors between the granulated and as-received powder from 1000 °C to 1500 °C.

3.6 Mechanical Properties

The mechanical tests were evaluated on the fully dense sample sintered at 1350°C. The respective hardness (Hv) of samples made from freeze granulated and as-received powders are 20.8 and 19.1 GPa. The respective fracture toughness (Kic) of samples made from freeze granulated and as-received powders are 3.8 and 3.4 MPa·m\(^{1/2}\). The growth in mechanical properties from the as-received powder to freeze granulated powder could be attributed to the more homogenous final microstructure [21-22].
4. Conclusions

In this work, spray freeze granulation of submicron alumina with high purity is performed to explore the possibility of industrial-scale production of dense alumina via spark plasma sintering. Sedimentation is adopted to remove agglomerates and impurities. The combination of middle-sized granules (36 $\mu$m $<$ d $<$ 150 $\mu$m) and small-sized granules (d $<$ 36 $\mu$m) leads to a fine absorption mode between small granules and big granules, which is supposed to be beneficial for granule deformability. The comparison of sintering behaviors between granulated and as-received powder shows that the process of freeze granulation could avoid agglomeration and leads to more homogenous microstructure with little agglomeration in the particle packing, which resulted in better sinterability of alumina compact. Moreover, The Vickers hardness (Hv) increases from 19.1 to 20.8 GPa while the fracture toughness (K IC) increases from 3.4 to 3.8 MPa$^{\frac{1}{2}}$ by mean of freeze granulation.

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5. References

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Садржај: Спреј фриз гранулација је побољшан метод заснован на спреј гранулацији, који решава многа ограничења те методе. У овом раду, спреј фриз гранулација субмикронске алумине је рађена да би се истражила могућност индустријске производње густе алумине спарк плазма синтеровањем. Припрема праха као што су седиментација и одабир гранула одређене величине је потребна ради максималне употребе у индустријској производњи. Грануле су десификоване спарк плазма синтеровањем и коментарисане су величине као што су згушњавање и брзина згушњавања. Поређење синтерабилности гранулисаног и почетног праха је извршено ради провере улоге спреј фриз гранулације у згушњавању алумине. Викерсова тврдоћа (Hᵥ) и жилавост (Kᵢc) гранулисаних узорака је већа од почетних не гранулисаних узорака услед хомогеније микроструктуре и мање агломерата у праху након гранулације.

Кључне речи: алумина; спреј фриз гранулација; спарк плазма синтеровање